

Communication

Discovering Partially Charged Single-Atom Pt for Enhanced Anti-Markovnikov Alkene Hydrosilylation

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Discovering Partially Charged Single-Atom Pt for Enhanced Anti-Markovnikov Alkene Hydrosilylation

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Supporting Information

ABSTRACT: The hydrosilylation reaction is one of the largest-scale application of homogeneous catalysis and is widely used to enable the commercial manufacture of silicon products. However, considerable issues including disposable platinum consumption, undesired side reactions and unacceptable catalyst residues still remain. Here, we synthesize a heterogeneous partially charged single-atom platinum supported on anatase TiO₂ (Pt₁^{δ^+}/TiO₂) catalyst via electrostatic-induction ion exchange and twoan dimensional confinement strategy, which can catalyze hydrosilylation reaction with almost complete conversion and produce exclusive adduct. Density functional theory calculations reveal that unexpected property of $Pt_1^{\delta^+}/TiO_2$ originates from atomic dispersion of active species and unique partially positive charge Pt⁵⁺ electronic structure that conventional nanocatalysts do not possess. The fabrication of single-atom Pt1⁵⁺/TiO2 catalyst accomplishes a reasonable use of Pt through recycling and maximum atom-utilized efficiency, indicating the potential to achieve a green hydrosilylation industry.

The hydrosilylation reaction, the mild and atom-economic route for the formation of Si-C bond, is one of the most industrial process in silicon chemistry because of its widespread application in the commercial manufacture of organosilicon compounds.¹ Despite widespread application, homogeneous Pt-based catalysts still suffer from many considerable issues. Owing to unwanted isomerization, high-cost and energy-intensive purifications have to be carried out.^{1b,2} And the decomposition of catalysts usually gives rise to undesired side reactions and the coloration of products, which has significant deleterious effects on the quality of products and limit their applications, especially in medical supplies.³ Moreover, the disposable consumption of platinum not only contributes to high catalyst cost, but also results in appalling waste of scarce platinum resources. These drawbacks push the development of heterogeneous catalysts, featured with facile separation and recycling.⁵ However, owing to low efficiency of atom utilization or leaching of active species, current heterogeneous catalysts exhibit unsatisfying performance and limited stability.⁶ It is urgent but challenging to develop remarkable materials with

a combination of the advantages of homogeneous and heterogeneous catalysts.

Single-atom catalysts (SACs) have attracted significant research attention.⁷ Homogenized active sites and coordination environment, similar to their homogeneous analogues, make SACs idea bridges to connect homogeneous and heterogeneous catalysis.⁸ Furthermore, with full metal dispersity and maximum atom efficiency, SACs exhibit enhanced catalytic performance with low metal consumption.⁵ However, it is not easy to maintain atomic dispersion of active species under preparation and reaction against aggregation owing to high surface energy.^{7a,10} The spatial confinement of these species to prevent their mobile trend with the aid of suitable supports, such as cavities of MOFs and tunnels of zeolites, has been developed to address this issue.¹¹ Lamellar metal oxides are a class of tow-dimensional (2D) functional materials, consist of layers and abundant interlayer metal ions.¹² The subnanometer interlayer can efficiently trap active species in 2D spaces and interlayered ions can serve as a fence to further expand the adjacent distances of active species, assisting in restricting their agglomeration and maintaining atomic dispersion.





Inspired by great features of lamellar metal oxides, we develop a novel approach to accomplish synthesis of singleatom materials via an electrostatic-induction ion exchange and two-dimensional confinement strategy. As illustrated in Scheme 1, this strategy includes three steps: (1) inducing adsorption of the cationic metal complex onto the negatively charged 2D $Ti_3O_7^{2^\circ}$ sheets of titanate via electrostatic attraction and intercalation into the interlayers through ion exchange with interlayered ions Na⁺; (2) calcination for phase transformation and enhanced metal-support interaction; and (3) further reduction treatment to give the final Pt₁^{δ +}/TiO₂ catalyst. The Pt₁^{δ +}/TiO₂ containing Pt up to 0.58 % exhibit remarkable activity (100%) and optimal selectivity (100%) towards anti-Markovnikov alkene hydrosilylation. Density functional theory calculations reveal that excellent performance is attributed to atomic dispersion of active species and unique electronic structure of intermediate valence.

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Figure 1. (a) TEM image, (b) HRTEM image, (c) HAADF-STEM image and corresponding element maps, Pt (blue), Ti (green), O (red), respectively, and (d) AC HAADF-STEM image of $Pt_1^{\delta^+}/TiO_2$.

The titanate Na_xH_{2-x}Ti₃O₇ (x=0.75) nanotubes were firstly prepared based on our previously reported methods.¹³ As revealed by transmission electron microscopy (TEM) image in Figure S1, the obtain materials show multilayered tubular structure. In a typical synthesis of Pt1⁵⁺/TiO2, the cationic Pt complex [Pt(NH₃)₄]²⁺ was injected into acid aqueous solution containing titanate nanotubes, followed by stirring to induce adsorption of [Pt(NH₃)₄]²⁺ onto the negatively charged 2D $Ti_3O_7^{2-}$ sheets via electrostatic attraction. After ion exchange with interlayered Na⁺ ions, $[Pt(NH_3)_4]^{2+}$ was located between interlayers and confined by 2D Ti₃O₇² sheets and abundant interlayered ions. Then, the Ptintercalated titanate transformed into anatase TiO₂ via calcination in air at 400 °C, as confirmed by XRD peaks indexed to anatase TiO₂ (Figure S2). Followed by treatment at 160 °C in a 5% H₂/N₂ atmosphere, partially charged isolated Pt atoms were formed. To achieve electrostaticinduction ion exchange, selecting cationic complex as precursors is important, as supported by the presence of Pt nanoparticles in control sample by employing anionic PtCl₆²⁻ (Figure S3). As shown in TEM and high-resolution TEM (HRTEM) images of Pt1⁵⁺/TiO2 (Figure 1a and 1b), the tubular layered structure partially shrinks. The high-angle annular dark-field scanning TEM (HAADF-STEM) image indicates no obvious nanoparticles are observed (Figure 1c). As revealed by energy-dispersive X-ray spectroscopy (EDS), Pt, Ti and O elements are uniformly dispersed. Aberration-corrected HAADF-STEM (AC-HAADF-STEM) image demonstrates several isolated bright dots marked by yellow circles, corresponding to individual Pt atoms (Figure 1d).



Figure 2. (a) EXAFS FT spectra of $Pt_1^{\delta+}/TiO_2$, Pt foils and PtO₂. (b,c) EXAFS WT spectra of $Pt_1^{\delta+}/TiO_2$, Pt foils. (d) XPS spectra for Pt 4f of $Pt_1^{\delta+}/TiO_2$. (e) XANES spectra of $Pt_1^{\delta+}/TiO_2$, Pt foils and PtO₂.

To reveal the local structure of $Pt_1^{\delta^+}/TiO_2$, extended X-ray absorption fine structure (EXAFS) measurement and wavelet transform (WT) analysis were performed. Figure 2a shows the Pt EXAFS Fourier transform (FT) curves of $Pt_1^{\delta^+}/TiO_2$ and references. $Pt_1^{\delta^+}/TiO_2$ exhibits only one prominent peak at about 1.6 Å, associated with the first shell of Pt-O scattering. And no reflection from Pt-Pt contribution is observed, compared with FT curve of Pt foils. It well demonstrates the sole existence of atomically dispersed Pt in $Pt_1^{0^+}/TiO_2$. To further reinforce this finding, WT analysis of Pt EXAFS oscillations was performed (Figure 2b), which can provide powerful resolution in both k and R spaces.¹⁴ As illustrated by the WT contour plots of Pt foils and PtO₂ (Figures 2c and S4), the intensity maxima at 5.5 Å⁻¹ and 8.5 Å⁻¹ are ascribed to the Pt-O and Pt-Pt contributions, respectively. In the WT contour plots of Pt1⁵ ⁰⁺/TiO₂, there is only one intensity maximum at about 5.3 Å⁻¹ from the Pt-O contributions, while no intensity maximum near 8.5 Å⁻¹ indexed to Pt-Pt path is detected. Taken together with AC HAADF-STEM, EXAFS and WT analysis, it can be evidenced that Pt atoms are atomically dispersed in Pt1⁶⁺/TiO2 and stabilized by O atoms. The quantitative EXAFS fitting was performed (Figure S5), and structural parameters of Pt in Pt₁^{o+}/TiO₂ are listed in Table S1. For comparisons, the fitting results of Pt foils and PtO2 are displayed in Figures S6 and S7.

The oxidation state of Pt in Pt₁^{δ +}/TiO₂ was analyzed by Xray photoelectron spectroscopy (XPS) and shown in Figure 2d. The Pt 4f spectrum can be deconvoluted into two peaks at binding energies of 75.8 eV and 72.4 eV, corresponding to 4f_{5/2} and 4f_{7/2} level, respectively. The peak positions are between those of Pt (II) and Pt (0), indicating Pt atoms carry partially positive charge through electron tranfer between metal and supports owing to enhanced metal-support interaction. Further electronic structure can be verified by Xray absorption near-edge structure (XANES) spectra. The white line intensities feature associated with the oxidation state of Pt. As shown in Figure 2e, the white line intensity of Pt₁^{δ +}/TiO₂ is higher than that of Pt foils and lower than that of PtO₂, demonstrating the partial oxidation state of Pt. 1

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Figure 3. (a) The scheme of hydrosilylation reactions with 1-octene and (EtO)₃SiH. (b) Conversion (%) of 1-octene vs time for $Pt_1^{\delta^+}/TiO_2$, Pt NPs, and commercial Pt/C. (c) Corresponding TOFs obtained at 20% conversion of 1-octene.

When we applied $Pt_1^{\delta^+}/TiO_2$ to catalyze hydrosilylation of 1-octene as a representative substrate with triethoxysilane ((EtO)_3SiH) (Figure 3a), we find it achieves almost complete conversion and exquisite selectivity, which only anti-Markovnikov addition product triethoxy(octyl)silane is detected by gas chromatography-mass spectrometer (GC-MS) analysis (Figure 3b), and no obvious alkene isomerization is observed. The calculated turnover frequency (TOF) of $Pt_1^{\delta^+}/TiO_2$ is achieved as high as 780 h⁻¹ (Figure 3c). And it also exhibits excellent reusability (Figure S8). Moreover, the spent $Pt_1^{\delta^+}/TiO_2$ catalyst was fully characterized, indicating atomic dispersion of Pt atoms is well maintained (Figures S9-S12).

For comparison, Pt nanoparticles supported TiO_2 (Pt NP/TiO₂) was prepared and examined (Figure S13), which exhibits only 47% conversion of 1-octene with a low TOF of 136 h⁻¹ (Figure 3c). In addition, much lower conversion (38%) of 1-octene and TOF (67 h⁻¹) is observed over the commercial Pt/C.

In addition, we examined the alkene and silane scope of hydrosilylation reaction with $Pt_1^{\delta^+}/TiO_2$, and the results are presented in Table S2. 1-hexene can be well catalyzed with (EtO)₃SiH (entry 1) in nearly complete conversion, only displaying the corresponding linear anti-Markovnikov product. The functionalized terminal alkenes bearing ether (allyl glycidyl ether, entry 2) and ester (entry 3) are demonstrated to react successfully to obtain excellent selective target molecular. When the substituted alkene substrate is aryl ring, the desired product is achieved in 98% conversion and \sim 90% selectivity (entry 4). The amino-, hydroxyl- and chloricfunctionalized alkenes also are catalyzed smoothly in ~97% conversion and ~99% selectivity (entrys 5 to 7). Moreover, different tertiary silane types of hydrosilylation like HSiEt₃ and HSiCl₂Me (entry 8 and 9), can also work well with 1octene and provide 99% selectivity to relevant products in conversion of 97% and 96%, respectively.

Furthermore, density functional theory (DFT) calculation was performed to investigate structural and electronic properties of $Pt_1^{\delta^+}/TiO_2$ and understand reaction mechanism. Two catalyst models (Figure S14) were constructed to represent different aggregation of Pt species. Pt nanoparticle (Pt NP) represents the smallest 3D nanoparticle without TiO₂ support. $Pt_1^{\delta^+}/TiO_2$ represents the interfacial model of single atom on TiO₂ support (Figure 4a).

Figure 4b shows the electron density difference (EDD) plot of $Pt_1^{5^+}/TiO_2$. The electron density between Pt atom and their adjacent O atoms increases, indicating the formation of chemical bonds. Moreover, the EDD around Pt shows a typical *d* characteristic. A significant electron transfer occurs

from *d* state of Pt to TiO₂ support, leaving the electron density at Pt sites depleted compared with metallic Pt. The calculated Hirshfeld charge on Pt in Pt1^{δ+}/TiO₂ is +0.51 (Figure S15), revealing that Pt1^{δ+}/TiO₂ possesses unique partially positive valence electronic structure, consistent with the XPS and XAENS results. Kinetically, the excellent hydrosilylation performance of Pt1^{δ+}/TiO₂ catalyst may be attributed to the intrinsic nature of partially charged Pt (δ +) atoms. Since the partially charged Pt (δ +) electronic structure of Pt1^{δ+}/TiO₂ has been generated prior to reaction proceeding, it does not need to undergo an extra reduction process to form a lower oxidation state to initiate hydrosilylation reaction compared with other higher oxidation state platinum (IV or II) catalysts.^{6a,15}



Figure 4. (a) Optimized structure of $Pt_1^{\delta^+}/TiO_2$. (b) EDD plots of $Pt_1^{\delta^+}/TiO_2$. The positive (in red) or negative (in blue) region indicates where the electron density is enriched or depleted. (c) Reaction paths for hydrosilylation reactions on Pt NP and $Pt_1^{\delta^+}/TiO_2$. The gray, blue, light blue, red, and white balls represent Pt, N, Ti, O, and H atoms, respective-ly. To highlight the reaction sites, pink and green balls represent the C1 and C2 in CH₂=CH-CH₃, respectively.

As proposed by Chalk and Harrod,^{15a} the reaction mechanism of Pt-catalyzed alkene hydrosilylation consists of Si-H oxidative addition to Pt and alkene insertion into the Pt-H bond followed by Si-C reductive elimination. As shown in Figures S16 to S18, our results confirm that on both Pt NP and $Pt_1^{\delta^+}/TiO_2$, the Chalk-Harrod mechanism is more favorable than the modified Chalk-Harrod mechanism, where alkene inserts into the Pt-Si bond. The energy profiles of detailed reaction pathway along the Chalk-Harrod mechanism of two catalyst models are shown in Figure 4c. The energy barriers in the Si-C reductive elimination step are the highest, suggesting that the third step is the ratedetermining step of this reaction. For the rate-determining step, the atomic dispersion of isolated Pt atoms plays a key role in facilitating the Si-C reductive elimination (Figure S20). Overall, in the three elementary steps, energy barriers for Pt₁⁰⁺/TiO₂ are lower than those for Pt NP thermaldynamically. The calculated results are consistent with high activity and selectivity for $Pt_1^{\delta^+}/TiO_2$ observed in experiment.

In summary, we have developed a new and robust catalyst with partially charged Pt as single atomic sites on anatase TiO₂, which exhibits remarkable activity, optimal selectivity and excellent reusability towards anti-Markovnikov alkene hydrosilylation. The unexpected property of $Pt_1^{\delta^+}/TiO_2$ can be attributed to unique partially positive valence electronic structure and atomic dispersion of Pt species. The fabrication of $Pt_1^{\delta^+}/TiO_2$ achieves reasonable use of catalysts by reducing consumption of precious platinum through recycling and maximum atom-utilized efficiency in the form of single-atom Pt, demonstrating the potential to achieve a green hydrosilylation industry. This work provides a concrete example to demonstrate single-atom catalysts can be a bridge to realize the heterogenization of homogeneous catalysis.

ASSOCIATED CONTENT

Supporting Information

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Detailed experimental sections; figures; tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

Y. Chen, S. Ji, and W. Sun contributed equally to this work. **Notes**

The authors declare no competing financial interests.

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